ULTRAVIOLET BAND SPECTRA OF AsO AND AsO^+

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Plate V

ABSTRACT. The band spectrum of AsO was excited, in a heavy current discharge from a 4 K.V. transformer, using a quartz discharge tube with internal hollow nickel electrodes fed with a specpure sample of As_2O_3. Two new doublet systems of bands designated as $C-X^2\Pi$ and $D-X^2\Pi$, analogous to those reported by one of the authors (Lakshman 1960) in the case of SbO, were observed in the region λ 3100 – λ 2400 A°. The spectra were photographed on a Hilger medium quartz and E_1 quartz littrow spectrographs. Vibrational analyses of these systems were carried out leading to the following quantum formulae.

$$C-X^2\Pi: \quad \nu = \begin{matrix} 38057.1 \\ 37664.8 \end{matrix} \Big\} + 656.3(v'+\tfrac{1}{2}) - 4.85(v'+\tfrac{1}{2})^2 - 964.0(v''+\tfrac{1}{2}) + 4.50(v''+\tfrac{1}{2})^2$$

$$D-X^2\Pi: \quad \nu = \begin{matrix} 38805.9 \\ 37780.5 \end{matrix} \Big\} + 611.5(v'+\tfrac{1}{2}) - 3.338(v'+\tfrac{1}{2})^2 - 964.0(v''+\tfrac{1}{2}) + 1.50(v''+\tfrac{1}{2})^2$$

In addition to the above systems, a singlet system of bands was obtained in the region λ 2550 – λ 2200 Å. A vibrational analysis of this system gave the following constants.

ν_e 42601.1 cm^{-1}

ω_e' 777.0 cm^{-1} $\quad \omega_e'\omega_e' = 6.57$ cm^{-1}

ω_e'' 1100.4 cm^{-1} $\quad \omega_e''\omega_e'' = 4.878$ cm^{-1}

From the magnitude of the vibrational constants, it is concluded, that the emitter of this system is the hitherto unknown AsO^+ ion.

Detailed arguments are presented for assigning this system to AsO^+. The observed electronic states of AsO and AsO^+ are compared and discussed with those of the related molecules on the basis of M.O. electron configurations.

INTRODUCTION

Connelly (1934), Jenkins and Strait (1935), Shawhan and Morgan (1935) reported two doublet systems $A-X$ and $B-X$ of AsO, in emission, in various sources of excitation in the region λ3450 – λ2350Å. Vibrational analyses of these two systems showed that they have a common lower state identified as a $^2\Pi$ state, with a doublet splitting of 1026 cm^{-1}. That this state is the normal state of the AsO molecule, is confirmed by the observation of the B–X bands in absorption by Connelly. Of these two systems the A–X system consists of red degraded bands in the region λ3450 – λ2950Å while the B–X comprises of violet degraded bands in the region λ2800–λ2350Å. From the observed double-

double headed nature of the bands, each of the two systems was ascribed to a $^2\Sigma$- $^2\Pi$ transition

The present investigations on the spectrum of AsO in heavy current discharges were started with a view to obtain possible new systems analogous to the C X and D X systems of SbO previously reported by one of the authors (Lakshman 1960). This work has led to the analysis and identification of two new doublet systems designated as C—X$^2\Pi$ and D - X$^2\Pi$ of the AsO molecule and of a band system attributable to the molecule AsO$^+$ whose existence is spectroscopically hitherto unknown We describe below the experimental procedure and the results of detailed analysis of the ultraviolet band systems of AsO and AsO$^+$.

EXPERIMENTAL

The spectra were excited in a heavy current discharge from a 4K.V. transformer, using a quartz discharge tube with internal hollow nickel electrodes fed with a specpure sample of As_2O_3 Photographs of the spectra were obtained under (a) low pressure stagnant vapour conditions by closing a stop-cock connected in between the dicharge tube and the system of evacuating pumps and (b) low pressure flowing vapour conditions In the former case, the band spectrum of AsO was obtained in the region λ3500--λ2400 Å while in the latter case, a new group of bands attributed to the AsO$^+$ molecule was obtained in addition to the above Exposures varying from three to ten minutes on Hilger medium quartz and one to two hours on E_1 quartz littrow spectrographs were found adequate to photograph the spectra on Ilford Selo-chrome and Special Rapid plates The band heads were measured against iron arc standard lines, using a Hilger comparator

RESULTS

AsO : *New systems* :

In addition to the A$^2\Sigma$ X$^2\Pi$ and B$^2\Sigma$ X$^2\Pi$ systems of AsO analysed by previous workers, the spectra reproduced in Plate V Figs. 1(a) and 1(b), reveal new groups of red degraded bands in the region λ3100--λ2400 Å The new bands, start from the shorter wavelength side of the A X system, and partly occur in a region of overlap with the B- X bands The wave numbers, intensities, and the vibrational assignments for these bands are given in Table I.

Vibrational quantum formulae were derived for the Q—heads of the A— X and B— X systems by Connelly (1934) and also by Jenkins and Strait (1935).

We have observed that the new group of red degraded bands could not be fitted into the vibrational schemes of either of the two components of the A—X system. It seemed, therefore, reasonable to assume tha tthey constitute one or more new doublet systems of AsO molecule. A clue to the analysis of the new bands was obtained by the observation of progressions of bands, whose $\Delta G(v)$

TABLE 1

Wavenumber, intensity and vibrational assignments for the bands of $C-X^2\Pi$ and $D-X^2\Pi$ syxtems of AsO and $A^1\Sigma-X^1\Sigma$ system of AsO^+

Wave-number cm^{-1}	Int.	v′,v″	Wave-number cm^{-1}	Int.	v′,v″	Wave-number cm^{-1}	Int	v′,v″
AsO C	$X^2\Pi_{3/2}$		AsO D	$X^2\Pi_{3/2}$		AsO^+ $A^1\Sigma$	$X^1\Sigma$	
33477	2	1,5	33839	2	0,4	39195	5	0,3
33745	3	0,4	35703	3	0,2	40267	7	0,2
34395	3	1,4	36448	4	0,1	41348	5	0,1
34673	4	0,3	37256	2	1,1	42113	8	1,1
35028	1	2,4	37602	4	0,0	42439	4	0,0
35609	7	0,2	38209	4	1,0	42866	2	2,1
35958*	–	2,3	38807	2	2,0	43205	6	1,0
36257	2	1,2	39402	2	3,0	43957	5	2,0
36558	7	0,1	AsO D	$X^2\Pi_{1/2}$		44693	3	3,0
37202	6	1,1	36727	2	0,2	45420	3	4,0
37843	4	2,1	37674	4	0,1			
38159	9	1,0	38280	3	1,1			
38794	4	2,0	38630	3	0,0			
39422	2	3,0	39236	5	1,0			
AsO C	$X^2\Pi_{1/2}$		39834	6	2,0			
34716	3	0,4	40424	4	3,0			
35644	4	0,3	41010	3	4,0			
36583	0	0,2	41588	3	5,0			
37531	8	0,1						
38180	2	1,1						
38487	4	0,0						

* Coincides with an atomic line.

intervals agree closely with those of the ground state $X\,^2\Pi$ of the AsO molecule. A detailed analysis, has shown that the new group of bands in the region $\lambda3100-\lambda2400$ Å could be interpreted on the basis of two overlapping doublet systems of bands, having a common lower state, identified as the $X\,^2\Pi$ state of the AsO molecule. On this basis, the bands have been arranged into two vibrational schemes shown in Tables II and III. Table II refers to the scheme of classification of a doublet system designated as $C-X\,^2\Pi$. As the bands appear

single headed, they may be either the Q heads of a $^2\Delta(a)$–$^2\Pi(a)$ transition or the R—heads of a $^2\Pi(a)$ $^2\Pi(a)$ transition. Of the two possibilities, the former appears more likely as the upper state can be identified to be a $^2\Delta_a$ state from a comparison of this state with similar levels identified in NS, SiF and SbO. (See discussion below). As the corresponding bands of the two component systems are separated by ~970 cm^{-1} the upper state is a regular state and has a doublet splitting equal to 1026 970 = 56 cm^{-1}. The C X $^2\Pi_{\frac{1}{2}}$ component system consists of only the strong $v' - 0$ progression of bands. The bands heads of C X $^2\Pi$ system could be represented by the quantum formula

$$\nu = \left.\begin{matrix}38637.1\\37664\ 8\end{matrix}\right\} + 656\ 3(v' + \tfrac{1}{2}) - 4\ 85\ (v' + \tfrac{1}{2})^2 \quad 964\ 0(v'' + \tfrac{1}{2}) + 4\ 50(v'' + \tfrac{1}{2})^2$$

to within an accuracy of 3 cm^{-1}.

TABLE II

Vibrational scheme of band heads of the C $X^2\Pi$ system of AsO

v' \ v''	0	1	2	3	4	5
0	38487	37531	36583	35644	34716	
		956	948	939	928	
		36558	35609	34673	33745	
			949	936	928	
		649	—		—	
		644	648		650	
	—	38180		—	—	—
1						
	38159	37202	36257	—	34395	33177
		957	945			918
	—	—	—	-	-	-
	635	641	-		633	
	—	—	—	—	-	—
2						
	38791	37843	-	35958	35028	
		951			930	
	—					
	628					
	- -					
3						
	39422					

Table III shows the scheme of classification of band heads of the other doublet system designated as D—X $^2\Pi$. The analysis shows that the upper state D belongs to Hund's Case (b) and the lower state has a doublet splitting of 1026 cm^{-1}, which is identical with the doublet splitting of the $^2\Pi$ ground state. The bands

of this system also appear single headed and may be either the R—heads of a $^2\Pi(b)$ – $^2\Pi(a)$ transition, or the Q– heads of a $^2\Delta(b)$—$^2\Pi(a)$ transition.

The band heads of the two component systems could be represented by the quantum formula .

$$\nu = \left.\begin{matrix}38805.9\\37780.5\end{matrix}\right\} + 611.5(v'+\tfrac{1}{2}) - 3.338(v'+\tfrac{1}{2})^2 - 964.0(v''+\tfrac{1}{2}) + 4.50(v''+\tfrac{1}{2})^2$$

to within an accuracy of 3 cm $^{-1}$.

AsO ^{1} *A singlet system*

TABLE III

Vibrational scheme of Band heads of the $D\ ^1\Sigma - X^2\Pi$ system of AsO

v' \ v''	0	1	2	3	4
	38630	37674	36727	—	
0		956	947		
	37602	36648	35703	—	33839
	954	945			
	606	606			
	606	606			
	39236	38280			
1		956			
	38209	37256			
	953				
	598				
	598				
	39834				
2	38807				
	590				
	595				
	40424				
3	39402				
	586				
	—				
	41010				
4	—				
	578				
	—				
	41588			—	
5	—				

As was mentioned previously this system of bands was obtained in the region $\lambda 2550$—$\lambda 2200$ Å when the vapour of a sample of As_2O_3 was kept flowing under low pressure conditions. It is reproduced in Fig 1(c) of Plate V. The wave numbers, intensities, and the vibrational assignments for these bands are shown in Table I. The analysis of this system presented no difficulty. The two

progressions of bands $v'' = 0$ and $v' = 0$ were easily identified leading to the vibrational scheme displayed in Table IV. The following vibrational constants have been derived.

$$\nu_e = 42601.1 \text{ cm}^{-1}$$

$$\omega_e' = 777.0 \text{ cm}^{-1}$$
$$\omega_e'' = 1100.4 \text{ cm}^{-1}$$
$$x_e'\omega_e' = 6.57 \text{ cm}^{-1}$$
$$x_e''\omega_e'' = 4.878 \text{ cm}^{-1}$$

TABLE IV

Vibrational scheme of AsO[1] bands

v'' / v'	0	1	2	3
0	42439	41348	40267	39195
	1091	1081	1072	
	766	765		
1	43205	42113		
	1092			
	752	753		
2	43957	42866		
	1091			
	736			
3	44693			
	727			
4	45420			

The singlet structure of this system and a comparison of the vibrational constants of this system with those of NO[1] and PO[1] indicate that the emitter of this system is the hitherto unknown AsO[1] ion. A detailed discussion on this is given in a later section.

DISCUSSION OF RESULTS

NO, PO, NS, PS, SiF, AsO and SbO.

We may now discuss the nature and properties of the electronic states of the AsO molecule in relation to those identified so far in the spectra of the related molecules NO, PO, NS, PS, SiF and SbO. Fig. 2 gives the term scheme of electronic levels identified till now. The ground state of these molecules is well known to be a $^2\Pi$ state and is represented as $X\,^2\Pi$. The levels A, B, C, D etc., are arranged in the order of increasing energy. However, the designation of the levels in PO and NO is not strictly in the order X, A, B, C etc. We notice for instance, that the first and second excited states of PO are represented by $B\,^2\Sigma$ and $A\,^2\Sigma$ respectively, while the $B'\,^2\Delta_i$ term in NO occurs in between the D and E levels, and the new C and D levels in AsO fall in between A and B. The ratio

of the vibrational frequency of an excited state with respect to the ground state viz. $\frac{\omega_e'}{\omega_e''}$ is shown on the right. It gives us a measure of the relative strength of binding of the excited state with respect to the ground state as the square of this quantity gives the value of $\frac{k_e'}{k_e''}$ from the relation $k_e = 4\pi^2 c^2 \mu \omega_e^2$ The values

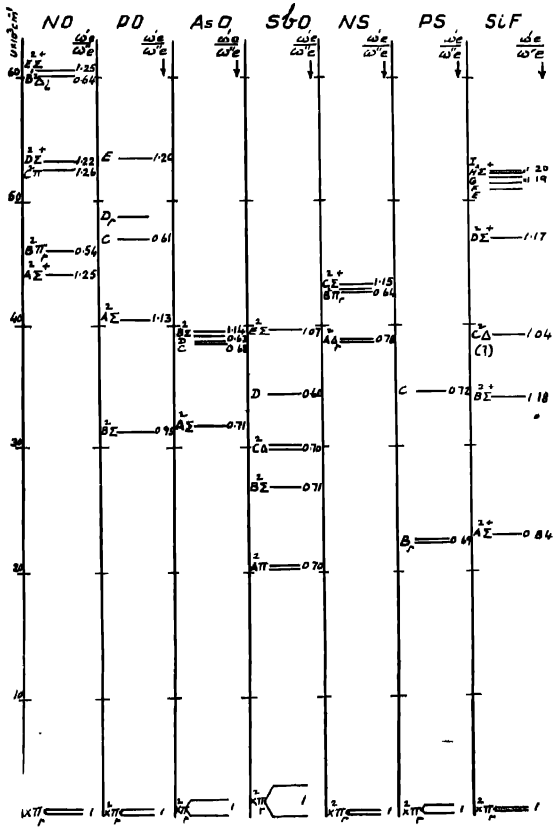

Fig. 2. Energy levels of NO, PO, AsO, SbO, NS, PS and SiF.

of $\frac{\omega_e'}{\omega_e''}$ and $\frac{k_e'}{k_e''}$ would be helpful in the identification of analogous states in the series of molecules referred above.

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PLATE V

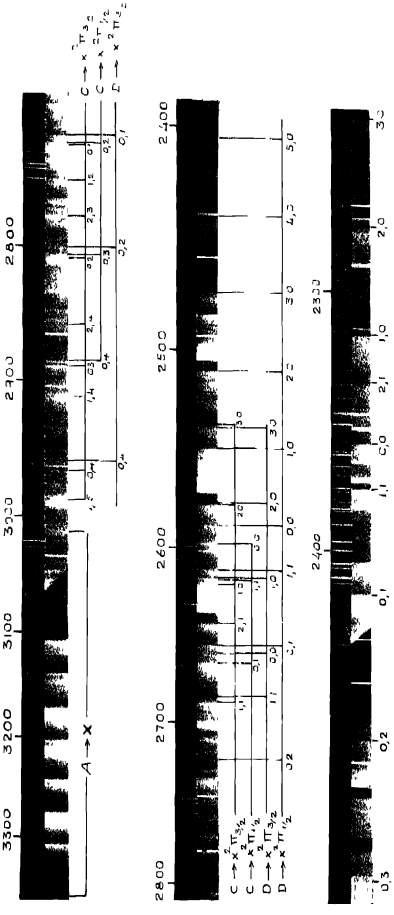

Fig 1. Medium quartz spectrograms.
(a) and *(b)* . The new C—X and D—X systems of AsO
(c) . The $A\,^1\Sigma$—$X\,^1\Sigma$ system of AsO^+
(The violet degraded bands in *(b)* and *(c)* belong to the B—X system of AsO)

The observed molecular electronic states of NO, NS, PO, PS were previously discussed on the basis of expected molecular electron configurations by Dressler (1955), and of NS and SiF by Barrow (1954 and 1958). Leaving the completed K and L shells, the ground state configuration in these molecules, in Mulliken's notation, is represented as

$$\ldots(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2(v\pi) \ldots {}^2\pi_r \qquad \ldots (1)$$

The results of a recent rotational analysis of PO by Singh (1959) and SiF by Johns and Barrow (1957) definitely show that the B level in PO $\left(\frac{\omega'_e}{\omega''_e} = 0.94\right)$ and A level in SiF $\left(\frac{\omega'_e}{\omega''_e} = 0.84\right)$ belong to a $^2\Sigma$ term. These states appear analogous to the $A\,^2\Sigma$ level in AsO $\left(\frac{\omega_e'}{\omega_e''} = 0.71\right)$ and $B\ ^2\Sigma$ in SbO $\left(\frac{\omega_e'}{\omega_e''} = 0.71\right)$ and belong to the excited configuration

$$\ldots(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)(v\pi)^2 \ldots {}^2\Sigma^+, {}^2\Sigma^-, {}^2\Delta, {}^1\Sigma^- \qquad \ldots (2)$$

The reduction in the vibrational frequency in the excited state of each of the molecules is due to the transition of an electron from the bonding $x\sigma$ orbital to the anti-bonding $v\pi$ orbital. However, as was mentioned by Dressler, the reduction in the vibrational fredquency of the $B\ ^2\Sigma$ state in PO is not so large as in others, indicating that the $x\sigma$ orbital in PO is practically non-bonding.

In addition to the $^2\Sigma$ state discussed above, the above configuration also gives rise to a $^2\Delta$ term. This state was identified with the B' level in NO by Miescher (1956) and with A level in NS by Barrow, Drummond and Zeeman (1954). A comparison of the values of ω_e'/ω_e'' for these states with the observed C levels in AsO and SbO (Lakshman, 1960) reveal that all of them are analogous. We may thus assign the C levels in AsO and SbO to a $^2\Delta$ term arising from configuration (2).

The vibrational analyses of the $C-X\ ^2\Pi$ in PO and of the $D-X\,^2\Pi$ system of AsO indicate that the upper state belongs to Hund's case (b). But the Λ—value of the state remains unknown, in the absence of the results of a rotational analysis.

The B level in AsO, E in SbO, C in NS and B in SiF are analogous states. Each of these states is characterised by an increase in the vibrational frequency and thereby the force constant with respect to the ground state. These states belong to the configuration

$$\ldots(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2 \ldots (\sigma) \ldots {}^2\Sigma^+ \qquad \ldots (3)$$

corresponding to the transition of an electron from a $\pi\pi$ anti-bonding orbital to a non-bonding σ orbital.

NO^+, NS^+, PO^+, PS^+ and AsO^+ :

In this section, we propose to give detailed reasons for assigning the singlet system reproduced in strip (c) of Plate V to the AsO^+ ion. The arguments presented in the following discussion are closely similar to those used by Dressler (1955) in the spectroscopic identification of the ions NS^+, PO^+ and PS^+. The justification for attributing this singlet system to the AsO^+ ion can be seen from the fact that there is a considerable increase in the vibrational frequency of the ground state term of the ion arising from the removal of the last $\pi\pi$ anti-bonding electron of configuration (1) representing the ground state of the neutral AsO molecule. We compare in Table IV the values of $\frac{\omega_e''\ (\text{Ion})}{\omega_e''(\text{Molecule})}$ and $\frac{k_e''\ (\text{Ion})}{k''\ (\text{Molecule})}$ for the pairs of molecules NO^+, NO, NS^+, NS; PO^+, PO, PS^+, PS, and AsO^+, AsO. We observe from the Table V that the values of $\frac{\omega_e''\ (\text{Ion})}{\omega_e'\ (\text{Molecule})}$ and $\frac{k_e''\ (\text{Ion})}{k_e''\ (\text{Molecule})}$ are exactly equal in the case of the three pairs of molecules given in the last three columns.

TABLE V

Comparison of the values of $\frac{\omega''_e\ (\text{Ion})}{\omega''_e\ (\text{Molecule})}$ and $\frac{k''_e\ (\text{Ion})}{k''_e\ (\text{Molecule})}$ for the pairs of molecules NO^+, NO; NS^+, NS, PO^+, PO; PS^+, PS, and AsO^+, AsO.

	NO^+ NO	NS^+ NS	PO^+ PO	PS^+ PS	AsO^+ AsO
$\frac{\omega_e''\ (\text{Ion})}{\omega_e''\ (\text{Molecule})}$	$\frac{2377}{1904} = 1.25$	$\times$ / 1219	$\frac{1405}{1233} = 1.14$	$\frac{845}{740} = 1.14$	$\frac{1100}{964} = 1.14$
$\frac{k_e''\ (\text{Ion})}{k_e''\ (\text{Molecule})}$	1.56	—	1.30	1.30	1.30

A similar comparison of the values of ν_e and $\frac{\omega'_e}{\omega''_e}$ and $\frac{k'_e}{k''_e}$ (given in Table VI) for the ions NO^+, NS^+, PO^+, PS^+ and AsO^+ also shows that there is a similar decrease in the strength of binding of the upper state relative to the ground state. The ν_e values of the singlet systems show the expected shift towards red with

TABLE VI

The values of ν_e, $\frac{\omega_e'}{\omega_e''}$, and $\frac{k_e'}{k_e''}$ for the molecules NO^+, NS^+, PO^+, PS^+ and AsO^+

	ν_e cm^{-1}	Transition	$\frac{\omega_e'}{\omega_e''}$	$\frac{k_e'}{k_e''}$
NO^+	73470	$A^1\Pi - X^1\Sigma$	0·68	0·46
NS^+	42000	$^1\Pi - X^1\Sigma$		
PO^+	49930	$A - X$	0·73	0·53
PS^+	40620	$A^1\Sigma - X^1\Sigma$	0·72	0·52
AsO^+	42600	$^1\Sigma - X^1\Sigma$	0·71	0·50

increasing value of μ, the reduced mass, as we pass from NO^+ and PO^+ to AsO^+. Since the ground state arises from the configuration

$$\ldots (z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2 \ldots {}^1\Sigma \qquad (4)$$

the upper state should therefore correspond to the excitation of an electron from either a bonding $w\pi$ or $x\sigma$ orbital to the $v\pi$ antibonding orbital. For molecules with small internuclear distance like NO^+ and NS^+ we may expect $x\sigma$ orbital to be higher in energy than $w\pi$. Thus the observed first excited $^1\Pi$ state arises from the configuration

$$\ldots (z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)(v\pi) \ldots {}^1\Pi \qquad \ldots (5)$$

However, for molecules with large internuclear distance like PO^+, PS^+ and AsO^+ for which the ratios are observed to be almost equal, we would then expect the $x\sigma$ orbital to be lower in energy than the $w\pi$ orbital. Thus the first observed excited state in these molecules may be represented by the configuration

$$(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^3(v\pi) \ldots {}^1\Sigma^+ \qquad (6)$$

Thus the singlet system of the AsO^+ ion may be represented by the transition $A^1\Sigma - X^1\Sigma$. This assignment of the transition is supported by the observed simple rotational structure of the bands consisting of only R and P branches when photographed under the high dispersion of a E_1 quartz littrow spectrograph. (2 Å/mm at λ2300 Å)

In his discussion of the electronic states of NO^+, NS^+, PO^+ and PS^+ Dressler (1955) has made the interesting observation that the vibrational frequencies of of the ground states of NO^+ and PO^+ agree closely with those of the excited states $A^2\Sigma$ and $A\ ^2\Sigma$ respectively of NO and PO as shown below

NO^+ : $\omega''_e = 2377$ cm^{-1} NO : $\omega'_e\ (A^2\Sigma) = 2375$ cm^{-1}

PO^+ : $\omega''_e = 1405$ cm^{-1} PO : $\omega'_e\ (A^2\Sigma) = 1391$ cm^{-1}

We have also observed that the vibrational frequency 1100 cm^{-1} of the ground state of AsO^+ agrees closely with the vibrational frequency 1098 cm^{-1} of the excited $B^2\Sigma$ state of AsO. Now, the $B^2\Sigma$ state of AsO was previously assigned to the configuration

$$\ldots (z\sigma)^2(y\sigma)^2(w\pi)^1(x\sigma)^2 \ldots (\sigma) \ \ldots \ ^2\Sigma$$

in which the last electron is in a non-bonding orbital. If this electron is removed in the process of ionization of AsO molecule in the $B^2\Sigma$ excited state, we should expect no change in the vibrational frequency of the ground state of the ion thus formed. This plausible explanation of the near equality of the vibrational frequency of the B state with the ground state of the ion gives additional support to the assumption that the emitter of this singlet band system is the AsO^+ ion.

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